SEPARATION OF MIXED POTASSIUM SALTS

BY

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ARMOUR INSTITUTE OF TECHNOLOGY

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Separation of Mixed Potassium Salts

A THESIS

PRESENTED BY

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TO THE

PRESIDENT AND FACULTY

OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

MAY 29, 1919

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A C K N O W L E D G M E N T.

I am greatly indebted to Professor H. McCormack for his helpful suggestions offered during the course of this work.

O B J E C T.

The object of this thesis is to determine the best method of separating, by fractional crystallization, the potassium salts contained in a mixture resulting from a potassium permanganate process. The desired purity of the separated salts is about ninety-eight per cent; they should be white and the crystals uniform. The separation must be commercially successful.

SOURCE OF MATERIAL AND PREVIOUS WORK.

The material from which the potassium salts are to be separated is the result of various attempts to prepare potassium permanganate on a commercial scale. The amount of potassium permanganate in the material from which it was to be recovered was insufficient for a commercially successful extraction. Most of the impurities present were potassium salts which in the pure state are of much more value. It was, therefore, desirable to recover and separate the various salts in as pure a condition as possible. The only commercial method of separating the salts is by fractional crystallization.

No written article on this special separation was found and perhaps no previous attempts were made. Some articles are published on general methods of obtaining the best separations by crystallization; and they proved to be of some value in this work. Some student work was done by groups on the separation, but the attempt was a failure.

FRACTIONAL CRYSTALLIZATION.

"Fractional Crystallization" is the separation by parts of two or more crystalline substance from a common solvent.

The efficiency of this process varies with the substances which are to be separated and is influenced by many conditions. The amount of substance which can be separated in the pure state depends upon the amounts of the substances in the solution, the difference in solubility of the substances at the same temperatures, the difference in solubility of each substance between zero degrees and the boiling point, and also whether the substances present have any effect on the solubilities of each other in the solution. The purity of the substance which separates depends upon the relative amounts of the salts present, the effect of substances present on the solubilities of the others, and the solubility of the salt which separates as compared with the others present.

It can be seen therefore that much information may be obtained from solubility data and that by means of a suitable curve or curves the best method of procedure could be developed. This, therefore, is the first thing to be obtained. The curves obtained from the data are often very complicated and unless one is familiar with such diagrams previously it is difficult to make the necessary deductions.

ANALYSIS OF MATERIAL.

The material is a very lumpy, heterogenous mixture of the various compounds. A well mixed sample has a dark greenish brown color when it is dry. The following is an analysis of the material after thorough mixing and sampling.

KNO_3	.....	41.76%
KCl	.....	36.70%
K_2CO_3	.....	8.34%
KOH	.....	0.0 %
$KMnO_4$	.....	3.55%
K_2MnO_4	.....	4.80%
MnO_2 - Insoluble	...	1.40%
Moisture	.....	3.15%
	TOTAL =	100.00%

The per cent. KNO_3 present was determined by difference inasmuch as there is no very accurate method of actually determining the amount present.

NECESSITY OF PRETREATMENT BEFORE SEPARATION.

By looking over the analysis of the material it may be seen that it consists chiefly of KNO_3, KCl, and K_2CO_3, which represent more than 85% of the material. These salts are all white. However since there is enough potassium manganate and potassium permanganate present to color the salts a deep purple they are undesirable impurities. Some method must be devised for destroying them without affecting the purity of the other salts present. It is desirable to recover the manganese as manganese dioxide, for by doing this all that remains in solution should be colorless.

Care must be taken in treating the material to get rid of colored compounds in order that the salts obtained will be as pure and white as possible. The solution obtained after removing the manganese should be colorless. If it is not colorless, all the manganese has not been removed and may precipitate out of the solution during

concentration. It was due to this difficulty that much time was required to get a colorless solution from which pure white salts could be crystallized.

Too much emphasis cannot be given to the care necessary in precipitating the manganese. Details such as time and temperature must be carefully observed. Care at this particular period of the process means much to the success of the separation of the salts at a later period.

PRETREATMENT.

The material first of all must be dissolved in the requisite amount of water. Insufficient water would mean a poor separation and too much water means a waste of heat and time to evaporate the eccess. The required amount of water may be calculated from the analysis of the material and the solubilities of the salts at the temperature concerned. The following table gives the amount of each salt and its solubility at the temperatures indicated, in grams per 100 cc. of water; and also the amount of water to dissolve it.

SUBSTANCE	T^{o}	SOLUBILITY.	T^{o}	SOLUBILITY.	WATER NECESSARY AT 100°C.
KNO_3-41.76gms.	0°C	13.3gms.	100°C	246.0gms.	16.98 cc.
KCl -36.7 gms.	0°C	28.5gms.	100°C	56.6gms.	64.90 cc.
K_2CO_3- 8.34gms.	0°C	47.2gms.	100°C	156 gms.	5.35 cc.
$KMnO_4$- 3.85gms.	0°C	2.83gms.	75°C	32.4gms.	11.87 cc.
K_2MnO_4-4.8gms.- decomposes					
MnO_2etc. 1.4 gms.					
Moisture - 3.15 gms.					
				TOTAL=	99.1 cc.

Therefore 99.1 cc. (approximately) are necessary to dissolve 100 gms. of the material. In this work 110 to 120 cc. of water were used depending upon the temperature to which the solution was to be heated.

After dissolving the salts in the required amount of water various solutions were used to precipitate the manganese in the form of manganese dioxide from the potassium manganate and permanganate. Two substances were used, alcohol and nitric acid. They were used in various quantities and in various proportions. It was a very difficult proposition to obtain a clear colorless solution after filtering out the manganese dioxide.

First of all, alcohol alone was used because it was thought that a strong acid like nitric acid would be undesirable to evaporate in iron kettles. Various amounts from 7 cc. to 70 cc. of alcohol to 500 gms. of salts were used. The filtrates obtained varied in color from dark

greenish yellow to pale yellow. The dark solutions during concentration became turbid owing to the separation of manganese dioxide. The results were not as satisfactory as they should be for the complete precipitation and separation of the manganese dioxide.

Mixtures of nitric acid and alcohol were then tried. A solution of 50 cc. nitric acid and 10 cc. alcohol diluted to three times its volume with water was added to a cold solution containing 500 gms. salts and 600 cc. of water. The solution was heated to boiling, filtered and an almost colorless solution was obtained.

Another mixture used was 40 cc. nitric acid and 5 cc. alcohol diluted as before. This gave a dark yellow solution. The solution which first went through the filter paper was practically colorless as before.

Another mixture used was 40 cc. nitric acid and 3 cc. alcohol which gave a filtrate that

became yellow on boiling.

Using a solution of 40 cc. nitric acid and 10 cc. alcohol a filtrate was obtained which was the most nearly colorless of all and it was decided at the time to use this mixture for the remainder of the work. After many solutions had been prepared in this manner and they varied in color from light to dark yellow and gave much trouble in getting a pure white salt, I decided to determine further the conditions which were best for precipitation.

It required 27 differently prepared samples to determine the best conditions and mixtures which would always give a filtrate that would be colorless. The conditions must be very closely adhered to in order to secure uniform and satisfactory resllts.

Sufficient water to dissolve all the salt should be used. To 1000 grams of salt 1165 cc. of water are added. This is heated to 180° to

190°F; or better, to boiling, and then cooled to this range of temperatures. To this is then added a solution of 20 cc. alcohol, 100 cc. water, and 40 cc. HNO_3 freshly and cautiously prepared, because of their interaction. The salt solution must be well stirred during the precipitation, after which it is then allowed to stand about an hour or more with occasional stirring. It is then filtered and refiltered if necessary to obtain a perfectly clear filtrate, and the precipitate is washed with small amounts of hot water to remove adhering salt.

It was soon discovered that the reason that the solution was colored was because all the manganese had not been removed from the solution. Then it was difficult to understand why it should all be precipitated; and then, on standing go into solution, which on concentrating reprecipitated. This was accidentally observed when an excess of nitric acid was added

to some colorless filtrate when a dark solution resulted with a strong evolution of chlorine. It was concluded that the chlorine dissolves the manganese in time and liberates it again when the chlorine is boiled out.

The results obtained when care is taken are entirely satisfactory and cause no trouble in obtaining the white salts.

METHOD OF SEPARATION.

After pretreating the salts only two salts remain, potassium chloride and nitrate. The problem is therefore to separate these two salts by crystallization. The approximate solubility of the salts at various temperatures should be known. The best method of observing the solubilities is by means of the solubility curves of the substances at various temperatures. By means of these curves some general ideas of separation may be obtained especially in this particular case where the curves are very different. It may be noticed in the solubility curves, Fig. 1, that the curves of KCl is practically a horizontal straight line while that of KNO_3 is a curved line, inclined more toward the vertical than that of the KCl. These curves, however, are true only when each substance is present alone.

The data is different when both are present in solution. The curves must be plotted differently than for the case of each salt separately. Thus,

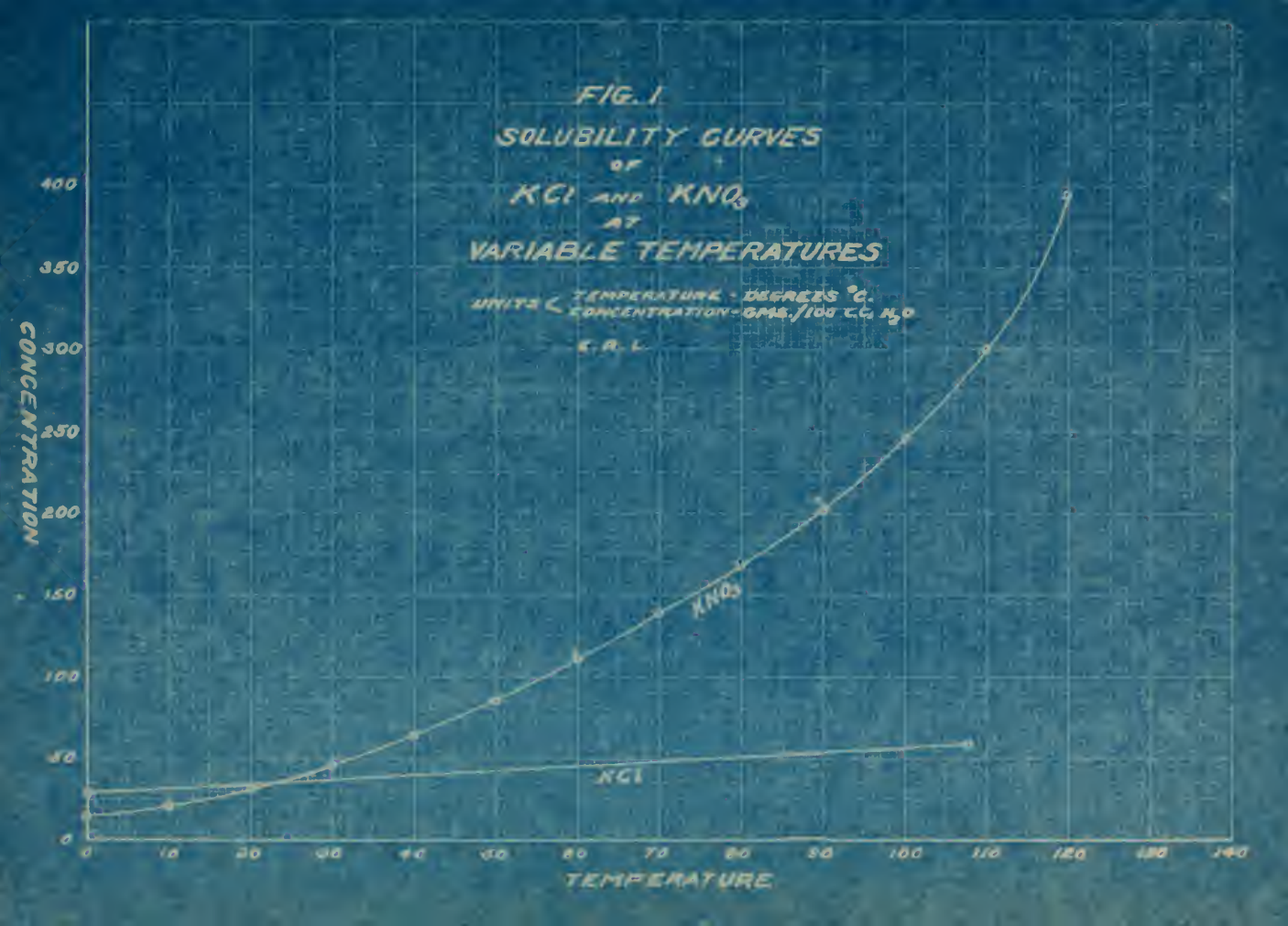
FIG. 1
SOLUBILITY CURVES
OF
KCl AND KNO3
AT
VARIABLE TEMPERATURES
UNITS { TEMPERATURE - DEGREES °C.
CONCENTRATION - GMS./100 C.C. H2O
C. A. L.
CONCENTRATION
TEMPERATURE
KNO3
KCl
0
50
100
150
200
250
300
350
400
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140

the axes used, Fig. II, represent the number of grams of the salts per 100 gms. of water. A series of curves may be drawn, one for each temperature because the solubilities change. There are but two curves plotted, for the temperatures of 20°, and 110° respectively; which represent the temperature of the room and the boiling temperature of the solution which is nearly constant. The points (C) and (F) are obtained from tables and straight lines are used to connect these points with (Y_1), (X_1) and (Y_2), (X_2) respectively. This is approximately true for all cases according to the written articles on the subject. The line Y_1CX_1 represents the saturation curve of the two salts at 110°C. The line Y_2FX_2 represents the saturation curve of the salts at 20°C. The point A represents the composition of the original solution after filtering out the manganese

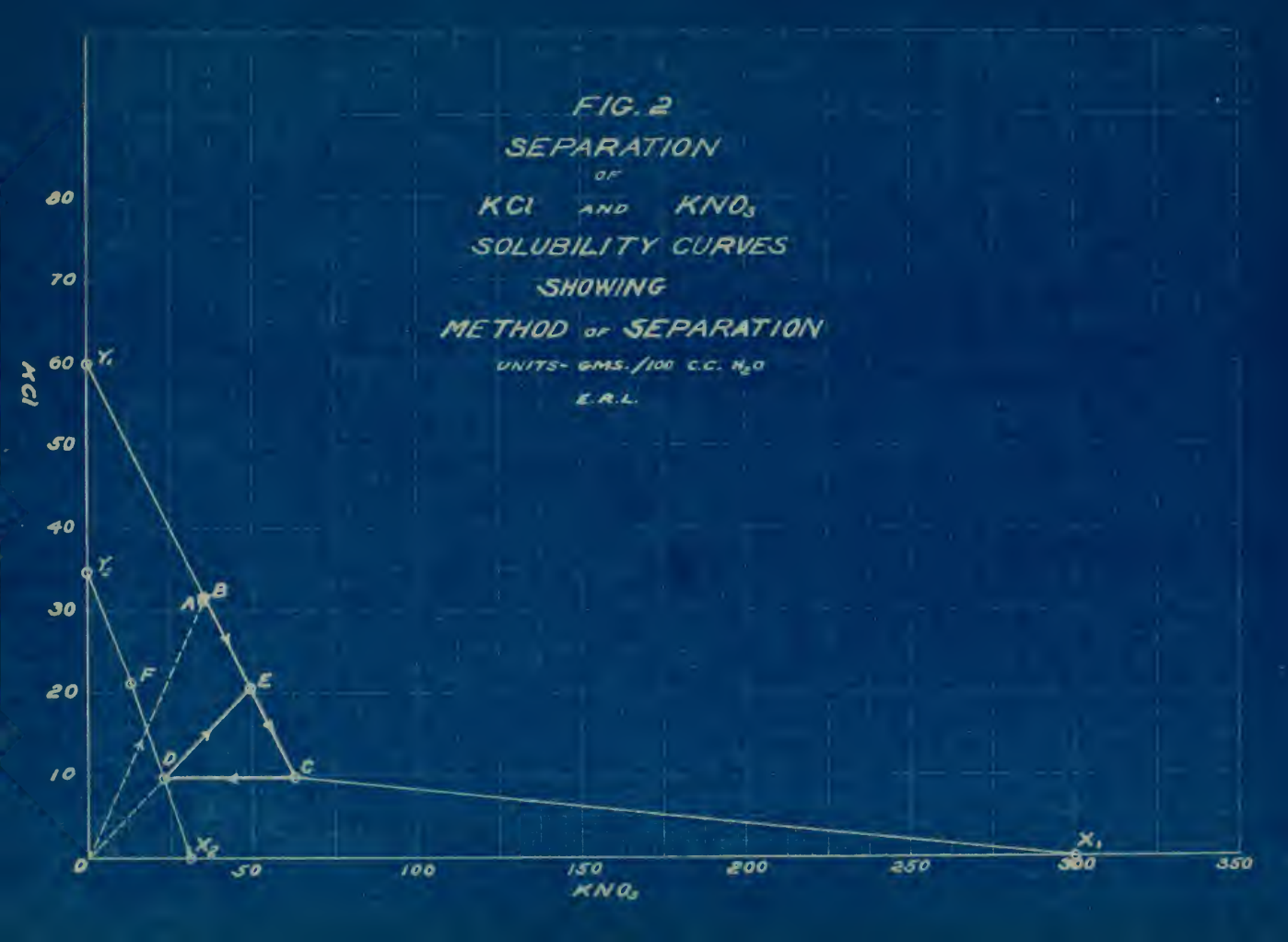
FIG. 2
SEPARATION
OF
KCl AND KNO3
SOLUBILITY CURVES
SHOWING
METHOD OF SEPARATION
UNITS- GMS./100 C.C. H2O
E.R.L.
KCl
KNO3
Y1
Y2
X1
X2
A
B
C
D
E
F
O
80
70
60
50
40
30
20
10
0
50
100
150
200
250
300
350

dioxide. The process which is followed is indicated graphically by the heavy line marked by arrows, which show the direction.

The point A represents the composition of the solution from which the salt is recovered, the co-ordinates of which are KCl - 31.5 gms. and KNO_3 - 36 gms. per 100 cc. of water. The solution is heated and concentrated at its boiling temperature until KCl begins to crystallize. In this period the relative amounts of KCl and KNO_3 in the solution remains the same. Therefore, the line passes from the origin (O) through (A) till it crosses the line YC which is the curve of saturation at 110° and here the solution becomes saturated with respect to KCl. The intersection of the two lines is represented by the pint (B). The solution is further concentrated at 110°C and KCl continues to separate out. The line which represents this operation is therefore the line BC. The KCl continues to separate until

the composition of the solution is that represented by the point C. At this point the KCl is filtered off from the solution at a temperature of 110°C. The filtrate is then allowed to cool to 20°C and the potassium nitrate which crystallizes out is filtered off. This operation is represented on the Figure by the line CD. The composition of the solution at D is represented by its coordinates. The process may be continued from D to E, C, D, etc., until all the salt is recovered. However, it was found by computation from the curves to be more economical to carry the process only from A to B, C, D.

The following figures show the theoretical yields obtained by means of the curves at the previous stages in the process.

POINT.	H_2O X cc.	KCl per 100 cc.	per X cc.	KNO_3 per 100 cc.
A	100 cc.	31.5 gms.	31.5 gms.	36 gms.
B	99 cc.	31.7 gms.	31.5 gms.	36.2 gms.
C_1	53.8 cc.	9.7 gms.	5.2 gms.	66.3 gms.
D_1	53.8 cc.	9.7 gms.	5.2 gms.	26.0 gms.
E	28.5 cc.	20.5 gms.	5.2 gms.	49.0 gms.
C_2	6.0 cc.	9.7 gms.	.6 gms.	66.3 gms.
D_2	6.0 cc.	9.7 gms.	.3 gms.	26.0 gms.

(Continued)

per X cc.	REMOVED.
36 gms.	
36 gms.	H_2O - 1 cc.
36 gms.	(H_2O-45.2 cc. (KCl-26.3 gms.
14 gms.	KNO_3-22 gms.
14 gms.	H_2O-25.3 cc.
14 gms.	(H_2O-22.5 cc. (KCl-4.62 gms.
5.5gms.	KNO_3-8.5 gms.

Theoretical Recovery to (D_1) - KCL =83.5% of total

" " " " - KNO_3=61.2% " "

Water Evaporated " " - H_2O =46.2 cc. of 100cc.

" remaining at " - H_2O =53.8 cc. of 100cc.

Theoretical Recovery to (D_2) - KCl =97.6% of total

" " " " - KNO_3=84.8% " "

Water Evaporated " " - H_2O =94 cc. of 100cc.

" remaining at " - H_2O = 6 cc. of 100cc.

KCl recovered from E to D_2 = 14.7% of total

KNO_3 " " E to D_2 = 23.6% of total

Water Evaporated = 47.8 cc. of 53.8cc.

Use of these figures could not be made except on the last run because the necessary data was not found until then. Better work could have been done if I would have had this curve and data as a guide to operations. Much time was used in trying to obtain the necessary data which I unknowingly possessed. The attempt was finally given up due to the lack of time and a means of better manipulation. The effort, however, revealed what turned out to be the best method economically of separating the salts.

SEPARATIONS AND RESULTS.

In the process of separation many difficulties arise. One of these difficulties is to find some means by which to tell when the potassium nitrate begins to crystallize with the chloride, in order that one may tell when to filter out the potassium chloride. The first method used was to observe the specific gravity of the solution by means of a hydrometer. This was unsatisfactory because the hydrometer is tossed about too much in the solution and also there is much danger of breakage. This method was discarded when it was found that the change in the boiling temperature was quite a good indication. A series of runs were made and much data obtained showing the reliability of the temperature indications. It was observed that the boiling point of the solution rose as it became more concentrated until KCl began to crystallize when the temperature remained constant for a long period

of time. Finally, the temperature began to rise quite rapidly. At the point where the temperature begins to rise, it was observed, is the time when potassium nitrate starts to crystallize out and the salt should be filtered out and the solution allowed to cool.

Another difficulty which arises is to wash the potassium nitrate liquid out of the potassium chloride crystals without dissolving too much of the chloride and also to wash the chloride solution out of the nitrate crystals without dissolving too much nitrate. This made it difficult to tell the purity of the salt.

Much data was obtained in order to see the accuracy which could be obtained by using a thermometer as a guide. Many runs were made to see if the results were consistent and satisfactory.

The data taken from one of the runs which was similar to the others is given in the following table starting with a kilogram and a half of the material.

TIME Minutes.	TEMPERATURE Degrees F.	CRYSTALS	VOLUME	KCl REMOVED
0	227.0°	No	1430. cc.	
10	229.0°	Yes	1415 cc.	
20	229.0°	"	1365 cc.	
30	229.0°	"	1350 cc.	
40	229.0°	"	1315 cc.	
50	229.0°	"	1285 cc.	
60	229.0°	"	1270 cc.	
70	229.0°	"	1230 cc.	110gms. KCl-98.4%
80	230.0°	"	1185 cc.	
90	230.0°	"	1150 cc.	
100	230.5°	"	1120 cc.	
110	230.8°	"	1080 cc.	
120	230.8°	"	1040 cc.	
130	230.5°	"	1000 cc.	
140	230.5°	"	970 cc.	
150	230.5°	"	925 cc.	190gms. KCl-98.5%

TIME Minutes.	TEMPERATURE Degrees F.	CRYSTALS	VOLUME KCl REMOVED.	
		C O N T I N U E D.		
160	233.0°	Yes	815 cc.	
170	233.5°	"	800 cc.	
180	233.5°	"	785 cc.	
190	234.5°	"	730 cc.	
200	235°	"	700 cc.	
210	236°	"	685 cc.	
220	236.5°	"	665 cc.	180 gms. 84.2%

The solution was then cooled rapidly and filtered. I obtained 400 gms. of KNO_3 which was 99.8% pure.

All of the salt obtained was not as pure as given but some of the salt was well washed before analyzing. This was done in order to be able to tell more closely what purity the salt was. It was quite impossible to get as high a yield as this with as high a purity by merely washing. However, indications are that the salts were pure

that crystallized at constant temperatures. It may be noted that after some salt is removed from the solution the constant temperature is slightly higher than before.

Figure 3 shows the results graphically, plotting time against temperature for each period before filtering. It is evident from the diagrams that the temperature may be used as an indicator of what is taking place. In the figure the lines A and D represent the time limits during which KCl alone crystallized. The line B represents the time at which the crystallized chloride was filtered out of the solution. The line C represents the time of the second filtration. The time for separating the chloride commercially is represented at D.

It must be understood that the rate of evaporation varies as it is dependent upon the amount of heat supplied per unit time.

By looking over the figures it may be seen that the temperature began to rise after 180 min-

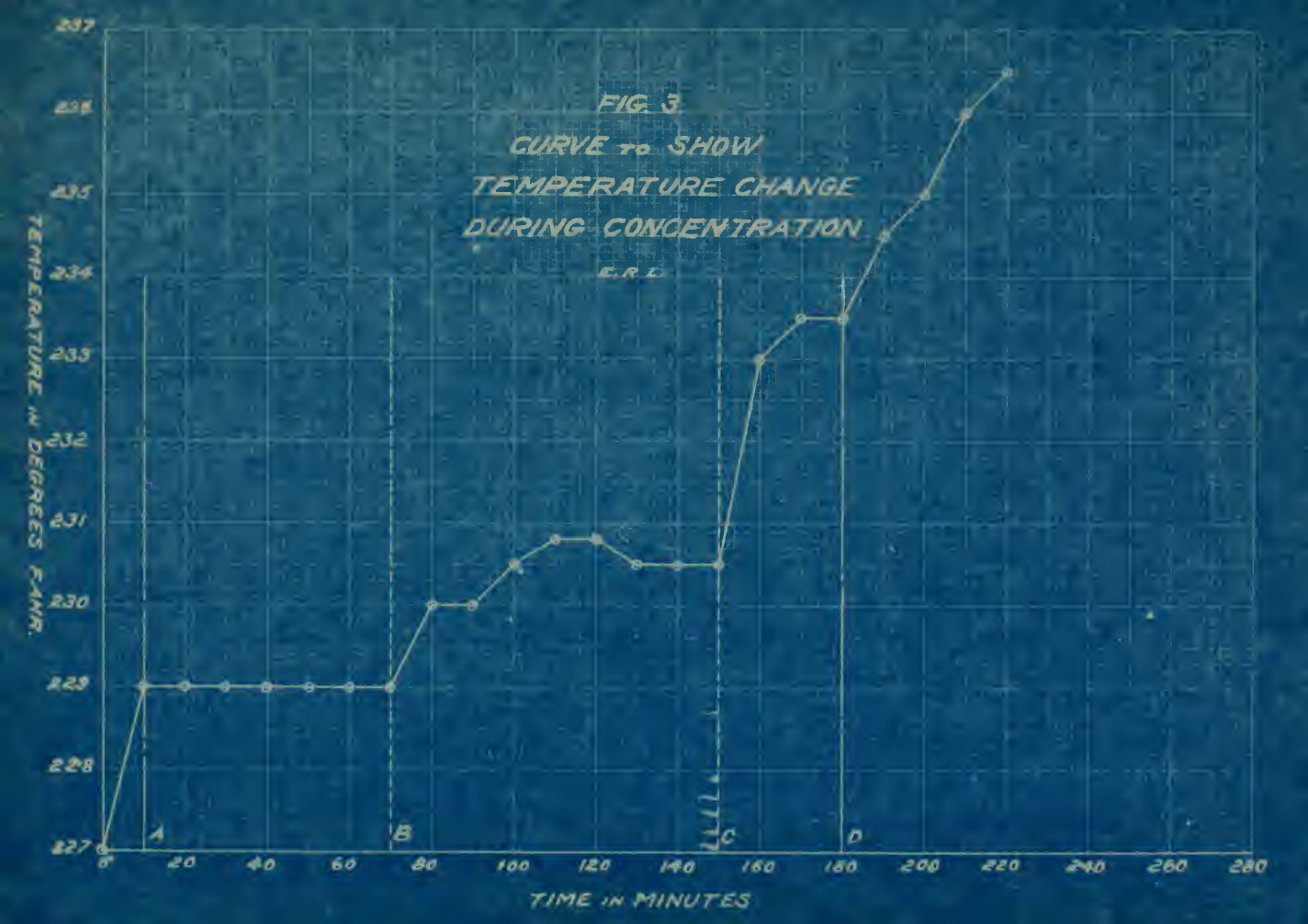
FIG 3
CURVE to SHOW
TEMPERATURE CHANGE
DURING CONCENTRATION
E.R.L.
TEMPERATURE IN DEGREES F.ANR.
237
236
235
234
233
232
231
230
229
228
227
A
B
C
D
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
TIME IN MINUTES

utes. At this point the volume was 730 cc. At the beginning of the run the volume was 1415 cc. The relative volume was then reduced to 51.6 cc. per 100 cc. which is 1.2 cc. lower than theoretical and is a fair check on results obtained from the curve.

Many complete runs were made also to separate the salt as completely and as pure as possible. The results obtained in the various runs were not as good as was expected. One of the reasons for this was the difficulty in manipulation, and the other was to get as much solution out of the salt as possible during filtration. This gave salts which contained too much impurity. More than the theoretical amount of the salt was obtained. The reason for this was that the crystals hold part of the solution which contains much impurity. 500 grams of salts retains about 100 cc. solution. All but the last run were completed without knowledge of the theoretical results.

One and one-half kilograms of material was used for recovering the salts. The solution was boiled down and the salt filtered out. It was washed twice with water and then dried, giving 510 grams of 82% KCl. Then it was again washed, filtered, and dried, and this left 400 gms. of 91% KCl. This was again washed, and dried, and 250 gms. of 95% KCl was obtained. It is evident that washing is not efficient enough to make it a success. The potassium nitrate in this operation was not recovered.

Using a new batch of material the process of recrystallization was employed and slightly better success was obtained. The results for this test may have been better if I would have known what the theory was. The chloride was filtered in a hot funnel and 850 gms. of wet KCl was obtained. In the dry state this would amount to about 725 gms. This was recrystallized, giving 450 gms. dry KCl which was 81.4% pure. This

yield, however, was not enough theoretically for 81.4% pure salt. The theoretical yield of 100% pure salt is 452 gms. The salt should also have been recrystallized again to determine the yield more correctly. Only 290 gms. of a possible 368 gms. KNO_3 was recovered and it was but 96.0% pure. About 650 cc. of solution remained.

The final run was made with the theory in mind. The purity was not as high as I expected. One and one-half kilograms of the material was used. After treatment the solution was concentrated observing the temperature and time. The following data was obtained.

TEMPERATURE	TIME	
221°	9:20	No Salt
224°	9:30	" "
226°	9:40	" "
229.5°	9:50	" "
230°	9:55	Salt Crystallizing
228°	10:00	" "
230°	10:10	" "
230°	10:20	" "
231°	10:30	" "
232°	10:40	" "
231.5°	10:45	" "
231.5°	10:50	" "
233.5°	10:53	" "
237.0°	10:55	" "

At 10:55 when the temperature rose to 237.0°, the crystallized salt was filtered out in the hot funnel. Six hundred-fifty grams of salt which analyzed 75.3% KCl was obtained; this is as much lower purity than usual. However, the theoretical yield of 100% KCl is but 452 grams.

The filtrate was rapidly cooled to obtain small crystals of nitrate. It was filtered at 20° and 425 grams of potassium nitrate obtained which was 89.6% pure. This is also much less pure than formerly; as high as 99.8% salt being obtained. Three hundred-sixty-five cubic centimeter of solution remained. The potassium chloride was recrystallized from a boiling solution and again filtered. It analyzed 82.5% and 520 grams were obtained. It was again recrystallized and I obtained 470 gms. of 84.7% salt. This was once more recrystallized and 450 grams of 89.2% salt was obtained, which is far less pure than was expected for as many crystallizations.

The potassium nitrate was also recrystallized from a cold solution and 370 grams of 97.8% nitrate obtained. This salt was not quite as pure as was expected, however, it was good enough considering that the yield was slightly more than theoretical.

From this process in all 650 cubic centimeters of solution was obtained which was saturated with respect to the nitrate at 20°. This solution contained 9.7 grams of KCl and 23 grams of KNO_3 per 100 cc. of water. It should be added to the next run in commercial practice.

PROPOSED METHOD.

Owing to a lack of time a method which combines the good yield of one method with the purer salts of another was not carried out as a unit. This method requires more time and operations and it is therefore not as economical, as the others.

A known amount of the mixed salts is treated as previously to remove the manganese from the solution. The clear colorless solution is concentrated until only a portion, about one-third, of the amount of pure chloride crystallizes. This should then be filtered out at the boiling temperature. The salt obtained after washing with small amounts of water should be about 98.5% pure. This was the purity of the salt obtained by this procedure previously. The filtrate and wash water should then be concentrated further until about the same amount of salt has crystallized. This is then treated as before. The filtrate and wash water are again concentrated further and separations made until the change of temperature takes place.

Then the filtrate is cooled to 20°C at such a rate that the crystals are about a half inch long. These are filtered off and washed with cold water. The crystals obtained should then be about 99.0 % or better.

The yield of both salts should be approximately theoretical. Some of the salt is dissolved during washing. The yield of KCl should be about 80% of the amount contained in the solution and the KNO_3 obtained should be about 50% of the amount contained.

CONCLUSION.

The experimental results obtained in this thesis were not entirely satisfactory. Whenever good yields were obtained the purity of the salts was lower than expected and vice-versa. Owing to a lack of time a proposed method which I am quite sure would give better yields and purer salts was not attempted.

The best potassium chloride obtained was 98.5% pure. It was white and free from noticeable impurities. The crystals were about the size of the head of a pin. The best yield obtained was about 82% of the total contained chloride.

The best potassium nitrate obtained was 99.8% pure. It was white and free from noticeable impurities. The crystals were about a quarter of an inch long and a thirty-second of an inch thick. The best yield obtained was about 60% of the total combined nitrate.

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